GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[x] ORIGINAL [ ] REVISION NO. _____

Project No. G-41-664 ~~GTRI~~/GIT DATE 4 / 23 / 84

Project Director: Dr. Robert A. Young School/~~Lab~~ Physics

Sponsor: DHHS/PHS/NIH/ National Institute of Dental Research, Bethesda, MD

Type Agreement: Grant No. 5 R01 DE01912-21

Award Period: From 5/1/84 To 4/30/85 (Performance) 7/30/85 (Reports)

Sponsor Amount:	This Change	Total to Date
Estimated:	$	$
Funded:	$ 187,284	$ 187,284

Cost Sharing Amount: $ 9,630 Cost Sharing No: G-41-342

Title: Tooth Enamel Apatite at the Atomic Level

ADMINISTRATIVE DATA OCA Contact Lynn Boyd x4820

1) Sponsor Technical Contact:

John D. Townsley, Ph.D.
Chief, Caries and Restorative
Materials Research Branch
NIDR-EP
(301) 496-7884

2) Sponsor Admin/Contractual Matters:

Robert Ginsburg
Grants Management Officer
Extramural Programs
NIDR
(301) 496-7437

Defense Priority Rating: n/a Military Security Classification: n/a

(or) Company/Industrial Proprietary: n/a

RESTRICTIONS

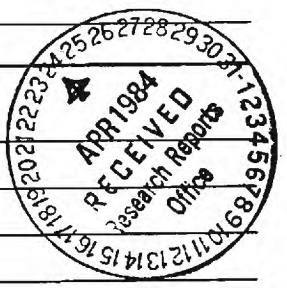
See Attached NIH Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT.

COMMENTS:

21st year of Grant.



COPIES TO:

Sponsor I.D. #02.108.001.84.015

Project Director	Procurement/EES Supply Services	GTRI
Research Administrative Network	Research Security Services	Library
Research Property Management	Reports Coordinator (OCA)	Project File
Accounting	Research Communications (2)	Other Newton

FORM OCA 4:383

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date June 5, 1985

Project No. G-41-664 School/~~xxx~~ Physics

Includes Subproject No.(s) N/A

Project Director(s) R.A. Young GTRC / ~~GTRI~~

Sponsor DHHS/PHS/NIH/ National Institute of Dental Research

Title Tooth Enamel Apatite at the Atomic Level

Effective Completion Date: 4/30/85 (Performance) _____ (Reports)

Grant/Contract Closeout Actions Remaining:

NOTE: Annual report submitted as a part of renewal application for G-41-659A.

- [ ] None
- [X] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Continues Project No. _____ Continued by Project No. G-41-659A

COPIES TO:

Project Director
Research Administrative Network
Research Property Management
Accounting
Procurement/GTRI Supply Services
Research Security Services
Reports Coordinator (OCA)
Legal Services

Library
GTRC
Research Communications (2)
Project File
Other Heyser

Jones

FORM OCA 69.285

G-41-664

SECTION IV
PROGRESS REPORT SUMMARY

GRANT NUMBER
DE-01912-22

PRINCIPAL INVESTIGATOR OR PROGRAM DIRECTOR
R. A. Young

NAME OF ORGANIZATION
Georgia Institute of Technology-School of Physics

PERIOD COVERED BY THIS REPORT
FROM: 15 Jan. 1984
THROUGH: 15 Feb. 1985

TITLE (Repeat title shown in item 1 on first page)
Tooth Enamel Apatite at the Atomic Level

(SEE INSTRUCTIONS)

PUBLICATIONS:

Full papers not previously reported as published.

P1. -"TSC Study of Electric Dipole Relaxations in Chlorapatite", N. Hitmi, C. LaCabanne, and R. A. Young, J. Phys. Chem. Solids 45, 701-708 (1984).

P2. -"The Structural Location and Role of Mn^{2+} Partially substituted for Ca^{2+} in Fluorapatite", P. R. Suitch, J.L. Lacout, A. Rewat, and R.A. Young (1985) Acta Cryst. (in press)

P3. "Infrared Determination of the Degree of Substitution of Hycroxyl by Carbonate Ions in Human Dental Enamel", J.C. Elliott, D.W. Holcomb, and R.A. Young (Submitted)

P4. "Optical Properties of Synthetic and Mineral Chlorapatites", J. C. Elliott (Submitted)

Two reprints of P1 are enclosed with the original of this application.

PROGRESS REPORT

1. General scientific goals: unchanged

2. Studies and results

In accord with the emphasis indicated on page 2., much of the work during the current reporting period has been directed toward trying to understand diffusion in the channels and various factors which might affect it. A report of That work comprises part 1 of the following three part report:

(1) Motion in the Channels
(2) CO_3 in Apatite and Tooth Enamel
(3) Substitutions in Apatites and Related Compounds.

(There are, of course, many such substitutions in tooth enamel apatite).

1a. F^- effect on diffusion. As has been reported previously, both short and long term studies have been carried out on the effect of F^- on diffusion along the channels, as measured by "deuterizability". Synthetic apatite made by the "reflux" method (hydrolysis of $CaHPO_4$) has been used for most of the studies because, like tooth enamel (TE), it contains both acid phosphate

and structurally incorporated molecular water. Our early studies pointed clearly to strong effect (diminution), but our extended studies involving many samples have resulted in an ambiguity which is yet unresolved. In the gross data, about half of the samples seem to show a significant inhibitive effect of the fluorine while the other half show none. To analyze the data properly, it is necessary to take into account the sizes and shapes of the individual particles. That may turn out to be a formidable task. During the reporting period, we have gathered full single-point BET surface area data on the specimens and the distributions of length/width ratios (from measurements on scanning electron micrographs) on representative samples. We are searching for a simple but acceptable way to incorporate this information in a data analysis method that will yield the true comparative deuteration rates. At the same time, other studies of motions in the channels have progressed much better.

1b. TSC studies. It was reported last time that the method of thermally stimulated currents (TSC) had been applied to apatites for the first time and that the results were very promising (see paper P1.). Dr. Hitmi (our collaborator) has now obtained TSC data for 11 apatites, including hydroxyapatite both with and without substitutions of chlorine, fluorine, and OD for OH. There clearly are reorientable electric dipoles at room temperature and they do become more readily reorientable with increasing temperature. Distributions of activation energies and relaxation times have been deduced from the data. It is expected that these will become important parameters in any successful mathematical model of diffusion along the channels.

Dr. Hitmi's thesis is rich with information that can be combined with information we have developed, and can develop, to produce new insights into apatites and tooth enamel. We expect to continue our collaboration with Dr. Hitmi to this end.

At the same time, Dr. Lacabanne's group in Toulouse (where Dr. Hitmi did her thesis) continues to collaborate with us and is currently developing TSC data on specimens of human tooth enamel supplied by us. The first, rather preliminary, results will be presented in our joint paper at the IADR meeting in Las Vegas, March, 1985. By the end of the summer, it will easily be time to prepare, jointly, the first paper for publication on TSC studies of human tooth enamel.

1c. Phase transition. There is developing evidence from the TSC studies, from the x-ray and dielectric studies of Rausch (1976), and the behavior of the OH librational band, in the infrared spectrum, with temperature that the reported monoclinic to hexagonal phase transition near 200°C in hydroxyapatite and chlorapatite is not driven by a simple order-parameter randomization [illegible]

phase transition is actually driven by the increased thermal energy of some other atom in the structure. If that is the case, then the motion of these other atoms must also affect diffusion in the channels.

1d.Neutron diffraction study of motions. We therefore collected high resolution neutron powdered diffraction data (at the Institut Laue-Langvin in Grenoble) on a deuterated reflux hydroxyapatite specimen at temperatures up to and through the reported phase transition temperature. We also collected room temperature data on an undeuterated reflux specimen and another hydroxyapatite prepared by high temperature methods in deuterated form. (The deuteration is desirable because of the large incoherent scattering cross section of hydrogen for thermal neutrons, which greatly increases the undesired background scattering.) With extensive Rietveld structure refinements, we have found no evidence for the OH ions becoming able to flip over (reorient) independently at the ~200°C phase transition.

Unfortunately, the standard deviations are too large to let us resolve all of the detail that we had hoped for in a straight forward structure refinement approach. As a consequence, we must work with one small part of the structure at a time and accept the risk that the results may be compromised by correlations with other parts of the structure. With this approach, we started systematically to "inquire" of the data whether some anisotropic thermal motions of either the Ca(1) or Ca(2) may be directly responsible for the phase transition and, therefore, for the reorientation of randomly chosen strings of OH's (or Cl's) at the ~200° phase transition.

We would like to have more and better neutron powder diffraction data which would yield more significant detail in the structure refinements. Whether we will be able to do that is debatable. We have already been fortunate to have had the use of the then currently best neutron diffraction instrument in the world, for the collection of the data just discussed.

1e. "Hot bands". We have undertaken a systemmatic study of the thermal behavior of the infrared hydroxyl bands (stretch, libration, and translation) to above 450°C. A so called "hot band" at about 3540cm^{-1} has been reported in the literature. This is, presumably, an OH stretch frequency shifted from its normal 3570cm^{-1} frequency by some OH ions finding a slightly different environment. The reported "hot band" is reversible. It occurs at essentially the same frequency as the fluorine perturbed OH stretch. We have found this "hot band" to be generally present and reversible, as reported, in hydroxyapatites but we do not find it in TE. Further, in two specimens we find the room temperature intensity of the 3540cm^{-1} band much too large to be explained by the amount of fluorine shown to be present by specific-ion-electrode measurements. A paper reporting our present results will be presented at the IADR meeting in Las Vegas, March, 1985.

1f. Carbonate. Our collaborative work with Dr. M. Vignoles in Toulouse has produced reasonable models for some of the "extra" infrared bands seen in the carbonate region of the spectrum between 1410 and 1570cm^{-1}. The new idea is that the CO_3^{2-} ion has distinguishably different vibrational frequencies (i.r.) according to whether it is accompanied by a vacancy or an F^- when it replaces a phosphate and whether it is neighbor to a vacancy an OH, or an F when it is in the channels (A site). Two joint-authorship papers should result from this work. One is now in preparation and the second will certainly benefit from face to face work on it planned for the first two weeks in September in Toulouse.

It was reported more than 20 years ago (e.g. Elliott, 1964) that a small fraction of the CO_3^{2-} in TE appeared to be in the A sites (i.e., in the channels). During this reporting period, we have attempted to quantitate that observation. With a TE specimen first heated to remove all carbonate and then recarbonated (A sites only), we have used a double beam i.r. instrument to balance out the amount of A-site CO_3 in untreated tooth enamel. We find that 11 (1)% of the CO_3 present is in the A sites. A paper on this work is now being accepted for publication (P3).

3. Substitutions in Apatites and Related Compounds. As is well known, the apatite in TE contains many minor substitutions for some of the atoms present in hydroxyapatite. It would, of course, be desirable to know exactly how each of these substituting ions affects it's immediate atomic environment in the crystal structure and how that, in turn, affects some easily measurable feature. In a collaborative effort with J. LaCout (Toulouse) and A. Hewat (Grenoble) we have been able to do this for Mn substituted at the level of about 3/8 atom per unit cell for calcium fluorapatite. With Rietveld structure refinements from neutron diffraction data, we have shown that the Mn substitutes (in specimens prepared this way) only for the Ca(1) ions, where it substitutes in a subset of such sites, thereby lowering the crystal structural symmetry and rotating the adjacent phosphate tetrahedra a bit. One Mn per cell interacts with, and thus rotates slightly, all six phosphate tetrahedra per cell. Thereby, the complete shift of the ν_1 phosphate i.r. frequency at 968 cm^{-1} to 959cm^{-1} by one Mn per cell is explained, as is the reluctance of the structure to accept more than one Mn per cell.

M. Taitai and J. LaCout in Toulouse have prepared a number of apatites in which the contents of the channels were varied from S_2 to zero by controlling the amount of europium substituted for calcium in the structure. With Rietveld x-ray structure refinements we have shown that the europium substitutes only for the Ca(2) and that the S occupies positions at 0,0,1/2 in the channels. These results, which are probably publishable as is or with only a little more work, are probably relevant to dental research as a contribution to the general understanding of the seemingly nearly infinite ability of apatite to accommodate

substitutions.

4. Future work. The work to be carried out during the next period is well foreshadowed by that reported here. A strong component will be our collaborative efforts with Dr. LaCabanne's group (TSC of TE) and Prof. Bonel's group (carbonate in apatite, other substitutions) in Toulouse, with Dr. Hitmi in Rabat (TSC, dielectric, and other physical studies of apatites with and without substitutions) and, possibly, Dr. Hewat in Grenoble (for more highest-quality neutron diffraction work). In our own laboratory, we will continue our studies of motions of various ions in the channels and the possible influences of out-of-channel ions on those motions. To this end, we are currently starting to collect further single-crystal x-ray diffraction data on chlorapatite as a function of temperature so that we may first study the effect of the changing thermal vibrational amplitudes of ions of one kind on those of other kinds. If that work turns out well, we may try to do a similar thing with the one or two monoclinic single crystals of hydroxyapatite which we have available. The purpose, as stated in the body of this report, is to disclose probable room temperature (or 37°C) effects of out-out-channel ions on activities such as diffusion within the channels.